

Prospecting for New Materials

J. M. Hill, M. P. Todd, G. T. Knoke, M. D. Fitzpatrick, D. C. Johnston



General Strategy and Motivation

Our synthesis work is driven by our group's goal to synthesize new and/or improved materials which exhibit novel or enhanced physical properties. The systems we study often arise through our earlier synthesis work and the results of our physical property measurements and modeling. An example of our synthesis efforts currently underway is described here, where the physics issues are outlined and the synthesis approach is motivated and described.

Metallic Spin Chains and Ladders

Background

- The high- T_c cuprate field spawned the study of spin-ladders, which itself became a full-fledged field of research after about 1993
- Over the past five years, DCJ and collaborators have experimentally and theoretically studied the magnetic properties of *undoped* copper oxide and vanadium oxide two- and three-leg spin-1/2 ladder compounds
- The most important conclusion from this work was that the presently accepted nearest-neighbor Heisenberg exchange model for the magnetic interactions in cuprate spin ladders and layers is inadequate, and that an additional four-spin cyclic exchange (or "ring exchange") interaction is likely important to the electronic properties

Motivations for the Present Work

- The experimental study of spin ladders is hampered by the dearth of model spin ladder compounds, particularly metallic ones. The only superconductor among these is $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$, which contains layers of Cu-O chains in addition to Cu-O two-leg ladder layers, complicating the interpretation of measurements. The maximum T_c is 12 K and the superconductivity only occurs under high pressure. There exist no superconducting, or even metallic, spin chain oxides of which we are aware
- Extensive theoretical and experimental studies have been made of the crossover from 2D properties to 3D properties as the layered high- T_c cuprates are doped and/or cooled, but little is known experimentally about 1D to 3D crossovers in metallic spin chain and spin ladder compounds.
- Little is known about the contribution of the ring exchange between Cu ions to the electronic properties of metallic 1D cuprate spin ladders and 2D cuprate layers

Primary Goals (Long-Range)

- Synthesize *metallic* spin chain and spin ladder oxides and study their physical properties. To date, there are few known examples of such materials. Several of many questions about them: Do they exhibit heavy fermion behavior, high- T_c superconductivity, novel magnetic ground states, and/or unusual electronic transport behavior?

This is part of our general search for novel or enhanced electronic, superconducting and/or magnetic behaviors in metallic oxides containing sublattices of localized magnetic moments

- By synthesizing metallic spin chain compounds and comparing their properties with those of spin ladder and spin layer oxides, it may be possible to evaluate the importance of the ring exchange interaction to the electronic and magnetic properties of low-dimensional transition metal oxides, since there can be no ring exchange in a spin chain material

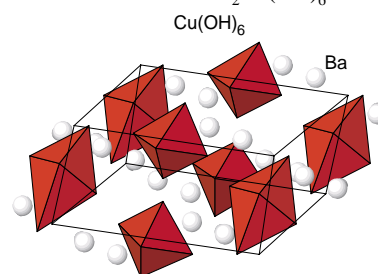
Example of a Compound and a Synthetic Method

- We are trying to dope the insulating $S = 1/2$ chain compound Sr_2CuO_3 into the metallic state using room-temperature electrochemical topotactic oxidation. This method was successfully used by our group to produce polycrystalline and single crystal superconducting samples of $\text{La}_2\text{CuO}_{4+y}$ ($0 < y \leq 0.12$) by oxidizing La_2CuO_4 in aqueous base. This method has the potential for producing single crystals of doped Sr_2CuO_3 , since single crystals of the parent compound can be grown.

Initial Results

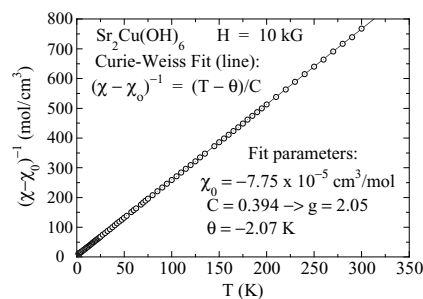
- In contrast to La_2CuO_4 , we found that Sr_2CuO_3 decomposes when exposed to water vapor or liquid water. The decomposition products are binary Sr and Cu hydroxides and the blue ternary hydroxide $\text{Sr}_2\text{Cu}(\text{OH})_6$. If CO_2 is present in the water vapor (e.g., in air) or is dissolved in the liquid water, SrCO_3 is formed as a decomposition product.
- To proceed with electrochemical synthesis of doped Sr_2CuO_3 , nonaqueous electrolytes must be utilized. Several of these are under consideration.
- We measured the magnetic susceptibility of monoclinic $\text{Sr}_2\text{Cu}(\text{OH})_6$, isostructural with $\text{Ba}_2\text{Cu}(\text{OH})_6$, which was synthesized separately in pure form. Our results (below) explain the previously known sensitivity of the magnetic susceptibility of Sr_2CuO_3 to the details of sample handling and heat treatment

Structure of $\text{Ba}_2\text{Cu}(\text{OH})_6$



- The $\text{Cu}(\text{OH})_6$ octahedra are isolated from each other: the magnetic coupling between Cu spins is expected to be weak

Inverse Magnetic Susceptibility of $\text{Sr}_2\text{Cu}(\text{OH})_6$



- The data confirm that the Cu spins $1/2$ behave as nearly isolated spins, with only very weak antiferromagnetic interspin coupling (≈ 2 K)

Other Ongoing or Planned Syntheses and Studies

- Synthesis of *metallic* fcc pyrochlore oxides and oxyfluorides containing d -electron local magnetic moments. Previous studies on such materials focused on insulators. We are attempting to find d -electron heavy fermion compounds to complement the one (LiV_2O_4) that we already found, using geometric frustration as a guiding principle, among metallic pyrochlores containing Mo ($S = 1$) or V ($S = 1/2$) local moments. An example is the hypothetical pyrochlore compound $\text{Lu}_2\text{V}_2\text{O}_6\text{F}$, which if it forms and is metallic will likely show interesting properties at low temperatures.
- Synthesis of large LiV_2O_4 single crystals and doped crystals is planned. Many experiments on this unique d -electron heavy fermion compound await such crystals
- Synthesis and study of MgB_2 -type superconductors in which the Mg is partially substituted by a magnetic d - or f -electron atom is in progress. Little is known yet about the influence of magnetic substitutions on the physical properties of MgB_2